

Review

Biochar for Water Pollution Control: From Sensing to Decontamination

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Abstract: Biochar, a biologically originated carbon-rich material derived from the oxygen-limited pyrolysis of biomass, is usually added to the soil for its enrichment, increasing its water-holding capacity and pH. This revolutionary material thus contributes to a reduction in the overall environmental impact and mitigation of climate change. Due to the beneficial properties of this material, especially for electrochemical applications (large active surface area, conductivity, etc.), biochar demonstrates an extremely high capacity for the adsorption and detection of micropollutants simultaneously. However, finding the optimal conditions for the adsorptive and electrochemical properties of prepared biochar-based sensors is crucial. The adsorption efficiency should be sufficient to remove pollutants, even from complex matrices; on the other hand, the electrochemical properties, such as conductivity and charge transfer resistance, are key factors concerning the sensing ability. Therefore, the balanced design of biochar can ensure both the usability and the effectiveness of sensing. To enhance levels of electroactivity that are already high, the pre- or post-modification of biochar can be performed. Such recycled carbon-based materials could be promising candidates among other electrochemical sensing platforms. In this study, different biochar modifications are presented. Utilizing important biochar properties, it should be possible to create a bifunctional platform for removing micropollutants from water systems and simultaneously confirming purification levels via their detection. We reviewed the use of biochar-based materials for the effective removal of micropollutants and the methods for their detection in water matrices.

Keywords: biochar; electrochemical sensor; micropollutant; decontamination; water



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1. Introduction

The growing global contamination of water systems with industrial or natural substances is one of humanity's key environmental problems. Most of these aqueous substances are present at low concentrations; however, their long-term contamination can provoke significant toxicological problems. Evaluating water quality requires the implementation of cost-effective and appropriate technologies for the efficient removal of micropollutants while ensuring the preservation of life-essential water components, such as the presence of individual minerals, etc. The development of such technologies often involves hazardous chemicals which are not eco-friendly [1]. Therefore, there is a pressing need for suitable "functional" ecological materials that can easily minimize the number of micropollutants in aquatic systems. Commonly used functional materials have significant disadvantages due to their dependence on fossil fuels and energy-consuming conditions for fusions. A renewable carbon-rich biomaterial that may represent a promising alternative to the other

carbon materials used in manufacturing equipment for water contamination has been proposed to address this issue. This material is the so-called “biochar” and is defined as a fine-grained carbon and ash-based bioproduct obtained by the anaerobic decomposition of biomass. Other substances, depending on the thermochemical conversion of (in)organic waste, are also present, such as a mixture of solids (biochar, charcoal, or carbon black), liquids (bio-oil), and gases (syngas). Biomass burning and their natural decomposition release large amounts of carbon dioxide (up to 50% of the biomass); however, the resulting solid carbon content becomes permanently stable. Highly porous biochar remains in the ground for centuries, which arrests the increase in atmospheric greenhouse gas levels. Biochar’s presence in the soil can improve water quality, increase soil fertility, raise agricultural productivity, and reduce the pressure on old-growth forests [2]. Carbonaceous material’s high porosity and large active surface area can determine its extremely high adsorption capacity. It is possible to benefit from these properties and implement biochar as a functional electroactive material to successfully determine a wide range of micropollutants in water matrices [3,4]. Therefore, the evaluation of the contamination levels of water systems can be achieved. Through its recycling as a material that can be used for electrode preparation, it has the potential to make a significant environmental contribution.

2. Treatment-Dependent Sorption Capacity of Biochar

Various ways of how to treat biochar can be applied as a pre- and/or post-pyrolysis modification, with the latter being more common (Figure 1). Post-pyrolysis modification involves treating the material after it has already been produced by physical or chemical methods. An example of physical modification can be steam-based activation, while chemical methods involve the application of acids and oxidizing agents or alkaline solutions. The main goal of modification is to enhance the quality of the material and remove its impurities, which leads to the formation of a better-performing adsorbent as well as a conductive electrode material [5]. Table 1 summarizes different procedures of biochar pyrolysis, showing the adsorption mechanisms, the properties of the biochar produced, and the applications of water decontamination.

2.1. Acid Modification

This method is most commonly performed with acids, such as hydrochloric, nitric, sulfuric, and phosphoric. Treating biochar with acids introduces more oxygenated functional groups, creating a more negatively charged surface that is an excellent adsorbent for positively charged analytes and, most commonly, metal ions [5,6]. The proton exchange on the biochar’s surface is the main principle of this mechanism. Another method of acid modification involves reducing the ash content and inorganic matter, creating a more porous material with a larger available surface, along with an increased hydrophobicity and aromaticity [7].

A more inexpensive but effective method of biochar modification utilizes hydrogen peroxide as an oxidizing agent. This method also introduces oxygen-containing functional groups that are beneficial for detecting various analytes; however, it has been reported to decrease the pH of the biochar [8]. The effects of hydrogen peroxide on biochar need to be evaluated based on target analytes, as it has been reported that it may dissolve minerals within the matrix of biochar, which are responsible for the adsorption of metal cations by precipitation mechanisms [9]. Like the acidic treatment, a higher H₂O₂ concentration leads to an increasing number of oxygenated functional groups on the biochar surface, thus increasing the ion exchange capacity. This consequence is beneficial if the analyte undergoes hydrogen bonding; otherwise, such functionalization is believed to weaken the overall dispersive forces of π – π interactions.

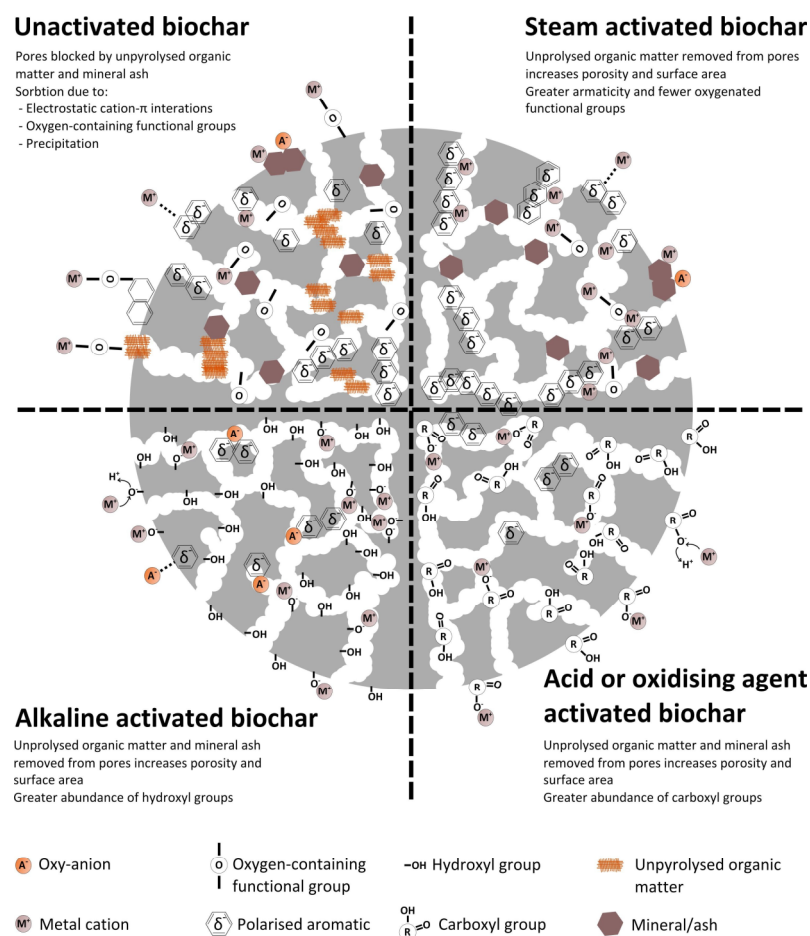


Figure 1. Different methods of biochar functionalization. Reprinted with permission from Ref. [5]. Copyright 2017, Elsevier.

2.2. Alkaline Modification

The effects of alkaline modification are similar to those obtained by acid modification and mainly rely on introducing oxygenated functional groups on the surface of the biochar, which can serve as proton donors for the adsorption of metal cations [10–12]. The most common modifiers are potassium and sodium hydroxide. Whether alkaline modification also positively affects the surface area of biochar relies on the type of feedstock and the conditions under which biochar is produced. There are reports of the surface area being dramatically increased by this type of modification, while others describe little to no change in the material [13]. Both acid and alkaline treatments provide enhanced adsorption due to the increase in the surface area. Unfortunately, these modifications may not have any selectivity to some micropollutants that do not create hydrogen bonding, similar to the H_2O_2 agent. A good example is the adsorption of methylene blue, which is fixed on the biochar surface via π - π interactions [14].

2.3. Modification with Metal Salts or Oxides

This type of modification can be realized in two ways. Either the feedstock is soaked in a metal salts/oxide solution before being pyrolyzed into the biochar, or the biochar product itself may be submerged in a solution to impregnate it with metal salts or oxides. Biochar-metal composites were proposed due to the unmodified biochar having a very weak affinity to anionic analytes because of its negatively charged surface and high pH. The introduction of metal compounds, and therefore the introduction of a positive charge into the structure of biochar, made it a viable adsorbent for the removal of contaminants containing negatively charged groups, such as NO_3^- , PO_4^{3-} and AsO_4^{3-} from aqueous

solutions, even though the overall surface area of the biochar was negatively impacted by embedding metal compounds into the material's pores [15,16].

2.4. Steam Modification

When high-temperature steam is forced through an interconnected web of micropores within the biochar, it can remove common contaminants, such as the remnants of unhydrolyzed organic matter, increasing the total surface area. This method may be beneficial for the sorption of some analytes while counterproductive for others, as it was found by Shim et al. [17], who reported a decrease in oxygen-containing functional groups on the surface. These findings conclude that steam activation is less effective than acid and base activations and combining it with other activation methods as a first step would be best.

Table 1. Summary of biochar pyrolysis, its properties, and applications for water decontamination.

Analyte	Biochar Feedstock, Pyrolysis Temperature	Driving Adsorption Mechanism	Adsorption Capacity [mg/g]	pH	Ref.
Paracetamol	Glucose, 900 °C	Pore-filling, H-bonding, n- π , π - π interactions	286	2–11	[18]
Paracetamol	Softwood, 550 °C	Van der Waals forces and H-bonding	40	6–9	[19]
Paracetamol	Municipal waste, 500 °C	Chemical reactions with oxygenated functional groups	33.3	2	[20]
Paracetamol	Pine chips, 300 °C	π - π interactions	N/S	6.5	[21]
Diclofenac	Waste sludge and leaves, 200 °C	Electrostatic interaction	877	6.5	[22]
Diclofenac	Plant waste, 600 °C	Pore-filling, van der Waals forces, π - π interactions	23.3	6	[23]
Diclofenac	Fish scales, 600 °C	Interactions with N, P, sp ² C, and C=O surface groups	967.1	1.5–4.1	[24]
Diclofenac	Sewage sludge, 600 °C	π - π interactions, H-bonding	92.7	3–4	[25]
Naproxen	Peanut shells, 800 °C	Pore-filling, π - π interactions	324	5	[26]
Naproxen	Sewage sludge, 600 °C	π - π interactions, H-bonding	127	2–11	[25]
Ibuprofen	Tamarind seeds, N/S	Chemical reactions with oxygenated functional groups	10.5	2	[27]
Ibuprofen	Pepper stems, 700 °C	Pore-filling, π - π interactions, H-bonding	569	4	[28]
Ibuprofen	Walnut shells, 450 °C	Pore-filling, π - π interactions, H-bonding	69.7	4	[29]
Ibuprofen	Alligator weed, 600 °C	Chemical and physical adsorption, not specified further	172	4	[30]
Caffeine	Tea waste, 700 °C	Electrostatic and nucleophilic interactions	15.4	3.5	[31]
Caffeine	Macrophytes, 750 °C	Chemisorption, not specified further	117.8	2–11	[32]
Caffeine	Pine needles, 650 °C	Electrostatic interactions	6.54	4	[33]
Caffeine	Sugarcane pulp, 850 °C	Pore-filling, π - π interactions, H-bonding	4.72	2–11	[34]
Caffeine	Pine needles, 900 °C	Chemical and physical adsorption, not specified further	11.85	N/S	[35]

Table 1. Cont.

Analyte	Biochar Feedstock, Pyrolysis Temperature	Driving Adsorption Mechanism	Adsorption Capacity [mg/g]	pH	Ref.
Malachite Green	Crab shells, 800 °C	π - π interactions, H-bonding	28140	6–8	[36]
Malachite Green	Chinese fan palm, 500 °C	N/S	21.4	7	[37]
Basic Red 46	Chrysanthemum flowers, 200 °C	Electrostatic and functional groups interactions, π - π interactions, H-bonding	53.19	7	[38]
Acid Orange 7	Mandarin peels, 150 °C	Electrostatic interactions	312.5	2	[39]
Acid Orange 7	Pea peels, 105 °C	Electrostatic interactions	523.1	2	[40]
Reactive Yellow 145	Nutshells, 400 °C	N/S	7.33	2	[41]
Indosol Black	Wood waste, N/S	Electrostatic interactions	185	2	[42]
Reactive Red 120	Microalgae, 600 °C	Electrostatic and surface groups interactions	331.9	<4	[43]
Acidic Blue 7, 120	Sewage sludge, 200 °C	N/S	99% removal	2	[44]
Eriochrome Black	Rice husk waste, 600 °C	N/S	94% removal	2	[45]
Congo Red	Orange peel waste, 700 °C	Electrostatic interactions	136	2–3	[46]
Congo Red	Leather shavings, 900 °C	Surface groups interactions	1916	7	[47]
Methylene Blue	Cardboard, 525 °C	Chemisorption, not specified further	25.1	6.5	[48]
Methylene Blue	Municipal waste, 300 °C	π - π interactions	7.2	5	[14]
Methylene Blue	Municipal waste, 500 °C	Electrostatic interactions	35	Unaffected	[20]
As (V)	Municipal waste, 600 °C	Electrostatic interactions, precipitation	28	6	[12]
As (III)	Rice husk, 700 °C	Formation of complexes between As and biochar surface groups	19.3	8	[49]
As (III)	Pine bark, 400 °C	Ion-exchange	13.1	5	[50]
Cd (II)	Sewage sludge, 900 °C	Ion exchange and surface precipitation	40	2	[51]
Cd (II)	Coconut shells, 400 °C	Ion exchange and surface precipitation	205	5	[52]
Pb (II)	Pinewood, 300 °C	N/S	4.25	5	[53]
Pb (II)	Cotton stalk, 650 °C	Chemisorption	147	2	[54]
Hg (II)	Wood chips, 600 °C	Formation of Hg-C(π) bonds, Hg interaction with carboxyl groups	107.5	6	[55]
Hg (0)	Municipal waste, 600 °C	Chemisorption and subsequent transformation of Hg ⁰ to HgCl ₂ by Cl-Cl bonds	0.16	N/S	[56]

3. Biochar-Integrated Sensing

Biochar has been used as an active layer for sensing in various forms, such as nanoparticles or as a part of carbon pastes. The combination of the biochar's adsorptive capacity and its electroactive properties can be utilized in the development of a sensing device where biochar serves as the electrode material. This ability increases the competitiveness between biochar and other carbonaceous materials that demand more complex and costly preparation steps. On the other hand, special attention must be given to the possible

interferences within the analysis since biochar is used as the electrode material. The main problem is the material's strong adsorption capacity, which leads to the registration of non-specific signals. Moreover, several compounds and elements can form complexes with biochar; therefore, the systematic evaluation of their interferences in the analytical performance of the electrochemical device must be considered. Until now, biochar-based sensors for the determination of molecules in food, environmental, and biological samples have been present (Figure 2). The percentual share of biochar-based sensing demonstrates the application of biochar as an electrode material for the determination of analytes in the field of food quality control (orange), water quality control (blue), and diagnostics (yellow). According to the Scopus database, most of them (69%) showed the application of these sensors in real water systems. Table 2 summarizes the application of biochar-based electrochemical sensors for detecting water micropollutants over the last few years.

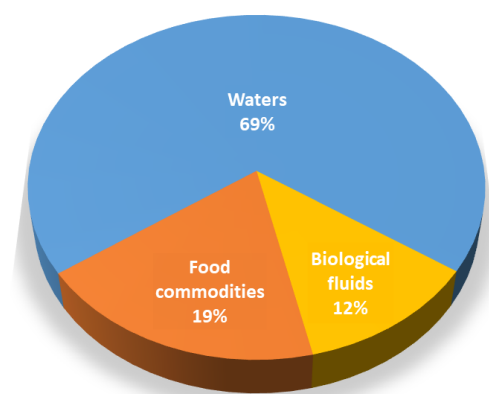


Figure 2. Share of application areas in biochar-based electrochemical sensors until now.

3.1. Conventional Carbon-Based Sensors

Another way to integrate biochar into electrochemical practice is its application to enhance the performance of traditional glassy carbon electrodes (GCE): arguably the most common electrode material. Dong [57] proposed a method for the preparation of biochar nanoparticles for the detection of 17 β -estradiol (EE2) on a modified GCE. This sensor was prepared by dropping biochar nanoparticles on the GCE surface. The electrode was then rinsed with distilled water and used for analysis (Figure 3a). Increased sensitivity was observed with binding biochar nanoparticles, which led to the appearance of the EE2 anodic peak at a potential of +0.67 V. Interestingly when optimizing parameters for the stripping analysis, biochar obtained lower pyrolysis temperatures and showed slightly higher adsorption capabilities (less than 2 mg difference). However, their amperometric response signal was much lower due to poor conductivity. This showed that while analyte adsorption could help improve the sensing signal, the main factor remained to have a highly conductive electrode surface. In addition, this approach indicated the important relation between the adsorptive and conductive properties of biochar nanoparticles. The adsorption of EE2 could occur via π – π interactions and hydrogen bonding, which depends on the functionalization of the biochar surface, as described in Section 2. When a good compromise in the biochar treatment was found, the adsorptive property significantly contributed to the molecular enrichment on the electrode and greatly enhanced the current signal of EE2. Therefore, a nanomolar detection limit was obtained in the proposed biochar nanoparticle-modified GCE, and this sensor was successfully applied to groundwater analysis.

Utilizing carboxymethyl cellulose as a dispersant and montmorillonite as a supportive compound to further stabilize biochar dispersions, seeing as their hydrophobic nature made them poorly soluble in water, Liu [58] proposed an aqueous solution for the pitch pine-based biochar that was used to modify GCE for the detection of cadmium ions. The sensor was prepared via the drop-coating technique on the electrode surface, and analyte detection was carried out via SWV stripping analysis. Contrary to statements made in

other works [59–61], chemical activation via an acidic or alkali medium (nitric acid, sodium hydroxide) was detrimental to the electrochemical response signal in this case. Untreated biochar-modified electrodes showed the highest peak current response to Cd ions.

Due to their highly conductive properties, biochar nanoparticles were selected as a signal enhancer for tyrosinase-based biosensors for sensitive bisphenol A detection, as suggested by Liu [62]. A composite mixture of biochar nanoparticles was mixed, and tyrosinase served as the modifier for the GCE, which was bound by Nafion polymer to homogenize the enzyme film. Other biosensors were created by exchanging biochar for multi-wall carbon nanotubes, graphite nanopowder, or graphene to evaluate the performance of biochar. Cyclic voltammetry (CV) was used to investigate the response of bisphenol A to the enzyme tyrosinase, which, upon reaction, created electrochemically active quinone. Out of all the prepared biosensors, the biochar-based one showed the highest response signal to bisphenol A., with the authors stating that this was not only because of the much larger surface area of the biochar compared to other modifiers but also due to the biocompatibility of the plant-based material, which supported the biocatalytic function of the enzyme bound to the electrode surface.

3.2. Carbon Paste Sensors

As mentioned above, the electrochemical properties of biochar could be significantly improved using an appropriate treatment method, such as metal doping. Wong et al. [63] were able to determine the herbicide glyphosate in river water utilizing the biochar and copper(II) phthalocyanine complex (CuHPc) as a carbon paste electrode (CPE) modifier. The BC-CuHPc complex served as an electron transfer enhancer on the electrode surface, leading to a current signal increase compared to CuHPc/CPE. The developed biochar-based sensor showed a linear concentration range of 0.3–4 μM and a limit of detection of 0.02 μM .

To increase the functionalization level of biochar, it is often pretreated with oxidizing agents with either strong acids or bases. Mostly, nitric acid is used for these purposes, as shown in Table 2. For instance, Roberto de Oliveira et al. [60] benefited from this theory and functionalized biochar using a strong acid-based pretreatment. They applied a biochar-rich carbon paste electrode that was activated with nitric acid to determine a pesticide, Methyl Parathion, in drinking water. The sensor showed good sensitivity and limits of detection, including 760 $\mu\text{A L/mM}$ and 39.0 nM, respectively. Good recoveries in tap water samples were obtained, which varied between 102 and 110% for three different concentration levels.

As follows from Table 2, the usual volume concentration of biochar used for the carbon paste preparation varied from 10 to 30% and had to be adequately homogenized. The rest was composed of a conductor (mainly graphite) and a binder (as mineral oils). Finally, the mixture was packaged on a suitable surface. Despite the electrode's advantageous properties, such as high stability, good selectivity, a long lifetime, and low cost, it is important to mention that the sensitivity varied depending on the type of material used, the pretreatment, the technique used, the electrolysis conditions, the electrolyte, and other factors.

3.3. Screen-Printed Sensors

As a sensitivity-increasing element, biochar can also be integrated into the development of screen-printed sensors. The modification of a screen-printed electrode is performed by dropping a biochar dispersion onto the working electrode surface (Figure 3b, down). This approach was used by Chen et al. [64], who developed a voltammetric sensor for the determination of trace leads in water with a wider linear range of 0.5–120 $\mu\text{g/L}$ (compared to an easily activated carbon-based sensor) and a detection limit of 0.02 $\mu\text{g/L}$. The lead ions were first deposited onto the biochar surface under optimized conditions, such as a deposition potential of -1.3 V and a deposition time of 300 s. Using square wave adsorptive stripping voltammetry (SWAdSV), the signal curves were registered upon dissolution, showing that the peak current of lead dissolution increased linearly with the increasing lead concentration (Figure 3b, up). For this purpose, hierarchical porous tubular biochar (PTBC)

was used. An aqueous solution of 0.3% Nafion and PTBCB was ultrasonically dispersed and dropped on the screen-printed electrode and composed of a carbon paste. The sensor was then in situ plated with a bismuth film and electrochemically characterized using CV and electrochemical impedance spectroscopy. The sensor sensitivity for the detection of lead ions was significantly improved after using the PTBC-based sensor. The PTBC sensor showed a much better analytical performance than ordinary activated carbon. In this case, the mesoporous structure of PTBC provided effective diffusion and mass transfer for many kinds of analytes, especially those which did not form any bonding or interaction with the functional groups on the biochar surface; therefore, the adsorption mechanism was only based on pore filling.

3.4. Innovative Biochar-Based Sensors

Currently, the paper has become an ideal platform for the fabrication of portable electrochemical sensing devices. Paper-integrated sensing systems are of interest due to their mechanical and chemical properties that allow a simple modification with nanomaterials and biomolecules such as immunoreagents or nucleic acids [65]. Yao [66] constructed an electrochemical immunosensor based on paper as a substrate for cyanotoxin microcystin-LR (MCLR) detection in water samples. This paper sensor was fabricated by a stable coating of highly conductive nanobiochar particles (nBC), which were obtained by the anaerobic pyrolysis of sugarcane waste at 800 °C and anti-MCLR monoclonal antibodies on filter paper via the dipping-drying method (Figure 3c). To block the active sites, bovine serum albumin was used. As indicated in the scheme, with an increasing amount of target MCLR, the current signal on the paper-based sensor was reduced, which was caused by blocking the electron transfer rate of the sensor upon binding MCLR to MCLR antibodies. The presence of MCLR was specifically quantified amperometrically with a response time of less than 5 min and the lowest detection limit of 17 pM. The nBC particles enhanced the electrochemical conductivity of the paper and showed the potential to be broadly applied to high-performance target analyte sensing.

Table 2. Application of biochar-based electrochemical sensors for the detection of water micropollutants.

Analyte	Matrix	Electrode	Treatment	Method	LOD [nM]	Ref.
17 β -estradiol	Water	GCE	HCl for BC NPs dispersion	CV, DPV	11.3	[57]
Bisphenol-A	Water	GCE	BC NPs	CV	3.18	[62]
Bisphenol-A	Tap and Ground Water	GCE	HCl for BC NPs and ZnO dispersion	DPV	100	[67]
Catechol	Tap Water	GCE	AuNPs decorated BC	CV, DPV	9	[68]
Catechol	Tap Water	GCE	AuNPs decorated BC	CV, DPV	4	[68]
Glyphosate	River Water	CPE	CuHPc integrated BC	SWV	20	[63]
Hydroquinone	Tap Water	GCE	AuNPs decorated BC	CV, DPV	3.4	[68]
Hydroquinone	Tap Water	GCE	AuNPs decorated BC	CV, DPV	2	[68]
Methyl Parathion	Potable Water	CPE	HNO ₃ oxidized 10% (v/v) BC	DPAdSV	39	[60]
Microcystin-LR	Tap, Lake, and River water	paper	Atb MCLR coated BC NPs	CA	0.017	[66]
Paraquat	Water	CPE	20% (v/v) BC	DPAdSV	7.5	[69]
Paraquat	Wastewater	CPE	HNO ₃ oxidized BC and rGO	DPAdSV	20	[70]
Cd (II)	River Water	GCE	Nanodiamonds and Chitosan modified BC	SWASV	110	[71]
Cd (II)	Industrial Wastewater	CPE	0–30% (v/v) BC	DPAdSV	69	[72]
Hg (II)	Tap Water	GCE	KOH activated BC on MOF film	DPAdSV	1	[73]
Pb (II)	Potable Water	SPE	Hierarchical porous tubular BC	SWASV	20	[64]

Table 2. Cont.

Analyte	Matrix	Electrode	Treatment	Method	LOD [nM]	Ref.
Pb (II)	River Water	GCE	Nanodiamonds and Chitosan modified BC	SWASV	56	[71]
Pb (II)	Industrial Wastewater	CPE	0–30% BC	DPAdSV	9.8	[72]
Pb (II)	Tap Water	GCE	KOH activated BC on MOF film	DPAdSV	1	[73]
Ni (II)	Discharge Water	CPE	HNO ₃ oxidized 15% BC	CV	250	[61]
Nitrite	Mineral and Tap Water	GCE	Eggshell membrane and copper ions modified BC	CV, DPV, CA	630	[74]

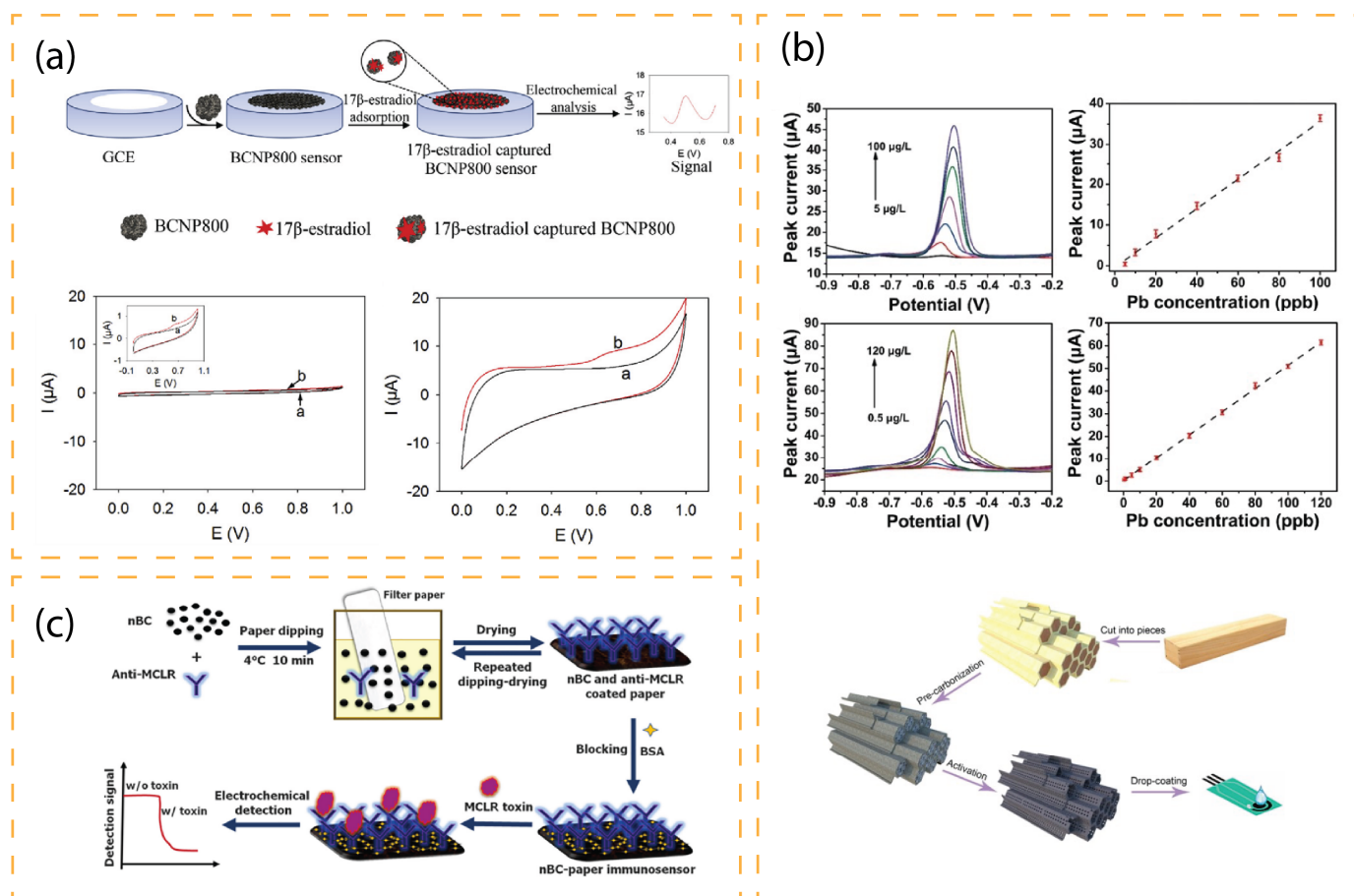


Figure 3. The step-by-step preparation of different biochar-integrated sensors based on (a) Conventional rod carbon electrode. Reprinted with permission from Ref. [64]. Copyright 2018, Elsevier, (b) Screen-printed electrode. Reprinted with permission from Ref. [57]. Copyright 2020, John Wiley and Sons, and (c) sensors with a paper substrate. Reprinted with permission from Ref. [66]. Copyright 2021, Elsevier.

4. Use of Biochar in Water Decontamination

One of the biggest challenges we currently face as humans is environmental pollution, especially the contamination of water—one of the most essential resources for life. Daily, millions of tons of pollutants are discharged into our world's water, creating extremely large amounts of wastewater. Emerging pollutants in wastewater management include a large group of inorganic (heavy metals and their compounds) as well as organic matters, such as pharmaceuticals, endocrine disruptors, surfactants, and UV filters used in sunscreens,

dyes, flame retardants, and others [75,76] (These micropollutants are generally present on the surface water and wastewater in the ng/L to µg/L concentration range).

Common water decontamination treatments include ozonation, ultrasonication, reverse osmosis, photocatalysis, chlorination, and the use of adsorbent materials [77]. Adsorptive removal has been deemed the most affordable and efficient way to rid the environment of these toxicants, utilizing adsorbents such as graphene, activated carbon, carbon nanomaterials, silica gel, activated alumina, and zeolites [76,78]. Many of the materials above are costly and challenging to produce, limiting their use in large-scale applications, which is why biochar has gained great interest mainly over the past two decades as an eco-friendly, effective, and affordable adsorbent to help combat emerging environmental concerns [79]. Below are several examples of successful applications of biochar to treat various groups of contaminants that are present within wastewater and environmental water.

4.1. Organic Pollutants

Absorption mechanisms for organic pollutants onto biochar typically include π - π interactions, n - π interactions, hydrogen bonding, electrostatic and hydrophobic interactions, as well as pore-filling and van der Waals interactions. Chemically, biochar predominantly comprises aromatic carbon rings with several types of oxygenated functional groups on the surface. The aromatic structure of biochar can form π - π stacking interactions with other phenol-containing compounds. Carboxylic and ketonic groups function as electron acceptors in donor-acceptor interactions. Given the large number of oxygenated groups on the surface, biochar is predominantly negatively charged, which can cause electrostatic interactions with positively charged molecules or ions and hydrophobic interactions [80,81].

4.1.1. Non-Steroidal Anti-Inflammatory Drugs

A primary area of interest within studies of biochar adsorption capabilities is the removal of pharmaceutical contaminants that belong to the non-steroidal anti-inflammatory drug family. Typical chemicals in this drug group include diclofenac, acetaminophen (paracetamol), ibuprofen, and naproxen. These pharmaceuticals, sold as over-the-counter pain relievers and used to treat various symptoms ranging from headaches to menstrual cramps, are abundant in environmental water sources and are continuously being found in increasing concentration [82].

One of the most frequently present drugs in the environment is paracetamol. It was found that paracetamol showed little to no change in adsorption capacity in pH values ranging from 2 to 10. It has been stated in the literature that paracetamol exists as an uncharged molecule within this pH range, which rules out the electrostatic interaction as one of the possible adsorption mechanisms of the analyte onto biochar [18]. For this experiment, two types of biochar were created. Traditional biochar, derived from pomelo peels, was pyrolyzed at 700 °C, and glucose-derived biochar was prepared with a two-step method of hydrothermal carbonization followed by pyrolysis at 900 °C. Morphologically, the glucose biochar exhibited a unique spherical structure composed of smooth microparticles that were similar in size. In contrast, the pomelo peel biochar showed a typical porous structure resembling the structure of a loofah. The biochar microparticles provided a significantly larger surface area, making more oxygenated functional groups on the surface that can be involved in the adsorption mechanism. Two mechanisms probably occurred: hydrogen bonding, as described in Section 2.1, which takes place due to the oxygenic surface, and pore filling since paracetamol is a small molecule. Adsorption onto the non-spherical biochar was driven mainly by pore filling. According to Fuentes et al. [83], the temperature also has little to no effect on paracetamol adsorption. Comparing the adsorptive efficiency of raw and acid-activated biochar efficiency, the tamarind seed-derived biochar was applied to remove ibuprofen from aqueous solutions [27]. Across all experiments, the chemically activated biochar showed a superior ibuprofen removal efficiency due to its increased surface and porosity. The removal of ibuprofen with modified biochar under optimized conditions (pH 2, 35 °C) reached 95%. The proposed material performed similarly after multiple cycles

of regeneration in methanol, showing excellent reusability, which made biochar applicable repeatedly. Adsorption was mainly driven by interactions between the carboxylic group present within ibuprofen and the hydroxyl, amine, and carboxyl groups on the surface of the biochar. Adsorption was greatly aided by a low pH value of two. The effective sorption of naproxen, diclofenac (anti-inflammatory drugs), and triclosan (antibiotic) with biochar derived from sewage sludge were also demonstrated [25]. Pyrolysis conditions and pH were leading factors influencing the effectiveness of the adsorption in these analytes. The optimal pH for the adsorption of diclofenac and triclosan was low, pH = 3, while the sorption of naproxen favored a pH higher than four but remained stable over a broad range. Higher pyrolysis temperatures produced a more porous biochar, which performed better in terms of adsorption, confirming pore-filling to be one of the mechanisms present in the process. Lastly, the authors state that the proposed biochar is no single-use and may be regenerated several times with methanol.

To confirm other works, similar findings on paracetamol adsorption were reported by Solanki and Boyer [19] and Sumalinog et al. [20], while Jung et al. [21] found that in multi-analyte systems, biochar favored naproxen over paracetamol due to strong hydrophobic interactions. Satisfactory diclofenac removal was also demonstrated by Zhang et al. [22], Xu et al. [23], and Xie et al. [24]. The adsorption of naproxen was independent of changing pH and NaCl additions, according to Tomul et al. [26]. The removal of ibuprofen, however, was strongly influenced by the pH, specifically for acidic conditions [28–30].

4.1.2. Stimulants

Caffeine is frequently found in environmental water at relatively high concentrations, which have been shown to rise every year due to the increasing rates of consumption of caffeinated beverages worldwide. Delivering a high solubility in aqueous media, caffeine remains detectable in water for extended periods due to its long half-life [31]. In this work, Keerthanam stated that caffeine is adsorbed most effectively to steam-activated biochar at an acidic pH of 3.5, mainly via electrostatic and nucleophilic attraction. At pH rates higher than 5.5, adsorption showed no dependency on pH. As previously mentioned, steam activation created more porosity within the biochar by eliminating the ash and remnants of unpyrolyzed organic matter, offering a higher adsorption capacity than pristine biochar. Several articles have also demonstrated the feasible adsorption of caffeine onto biochar [32–35].

4.1.3. Organic Dyes

Interactions between the biochar surface and various dyes causing adsorption are the same as for all organic molecules. Dyes can be classified into different categories, depending on their characteristic properties, such as acid (negatively charged), base (positively charged), direct, vat (natural indigo-derived), sulfur, reactive (anionic), disperse, or whether they can create metal complexes, such as anthraquinone, indigoide, triphenylmethyl, xanthene, and phthalocyanine derivatives. Based on these variations, choosing the adsorption process that would be the principal for micropollutant removal is complex. On the other hand, knowing the properties of the micropollutant in a monitored water system, an appropriate method of biochar treatment could be applied to achieve selective adsorption. The process of adsorption is influenced not only by the properties of the feedstock and the subsequent biochar product but mainly by pH, temperature, contact time, and agitation. For most dyes, a neutral to acidic pH is often optimum [84]. It is essential to consider the morphology of pores for any adsorbent when treating dyes, given as dyes vary massively in size, and even smaller dye molecules are still relatively large. Simply put, microporous adsorbents cannot capture large molecules regardless of their other material properties [85]. Biochar tends to be negatively charged, providing a natural affinity towards dye molecules with a positive charge [40].

As an example, biochar from several feedstocks have been prepared to study the applicability of this material for the adsorptive removal of dyes from aqueous solutions,

namely Malachite Green [36,37], Basic Red 46 [38]), Acid Orange 7 [39,40], Reactive Yellow 145 [41], Indosol Black NF1200 [42], Reactive Red 120 [43], Acidic Blue 7 and 210 [44], Eriochrome Black [86], Congo Red [46,47], and Methylene Blue [14,20,48].

4.2. Heavy Metals

As previously mentioned, biochar's composition, which results from feedstock choice and pyrolysis conditions and modification, is one of the leading factors affecting its properties as an adsorbent. Diversity in terms of porosity, specific surface area, cation exchange capacity, surface functional groups, and elemental composition ensures that no one method of biochar preparation is optimal for the adsorptive removal of every substance. Other factors affecting adsorption mechanisms, whether in aqueous solutions or soil, include pH, temperature, initial pollutant concentration, and biochar loading [86].

Heavy metal adsorption on the biochar in aqueous solutions is an endothermic process, meaning that it consumes energy. Therefore, increased temperatures facilitate this process. The effect of pH may be the most important in terms of heavy metal removal, as heavy metals tend to exist in the form of ions (such as arsenic, cadmium, lead, and mercury). Soil or water pH can affect the surface charge on biochar, impacting whether the material preferentially takes on cations or anions. Low pH values lead to the ineffective adsorption of cations. Additionally, the presence of coexisting ions commonly present in most aqueous environments, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , and SO_4^{2-} , leads to competition for adsorption sites and reduces removal efficiency. This is the case for any pollutant, not just heavy metals [87].

5. Perspectives in Real-Time Monitoring of Decontamination

The biochar figures as a bi-functional material for detecting and further decontaminating micropollutants by adsorbing them on its surface. For prospects, such material could serve as an active component in disinfection facilities for the general public, meaning that the study of biochar's excellent properties in both scientific and technological ways could lead to the development of a user-friendly product and its implementation in real life for the successful removal of micropollutants from water systems. Several studies have shown its great potential in next-generation energy storage as supercapacitors [88,89]. These devices could supply already-used technologies that are attributed to their multiple advantages, such as low cost/contamination, rapid charge/discharge capabilities, a long lifespan, and outstanding power density. Based on our knowledge so far on biochar, to this day, not so many research papers have been devoted to the idea that biochar could serve simultaneously as a sensor for pollution monitoring and a platform for real-time water decontamination, which would be favored by applying a potential (as seen in Figure 4). The presence of functional groups on the biochar-based electrode influences the capacitive properties, which leads to a different affinity in interactions with electrolytes and directly reflects on the size of the active surface area. Therefore, high-rate performance supercapacitors could significantly improve the adsorption rate and make the water treatment more effective.

However, some crucial aspects must be taken into consideration. A small gap exists between the optimal adsorption and electrochemical properties of prepared biochar-based sensors (Figure 3). The adsorption efficiency should be sufficient enough to remove the pollutants even from complex matrices. On the other side, the electrochemical properties, such as conductivity or charge transfer resistance, are key factors for the sensing properties. Generally, the biochar oxygen content and particle size have been shown to impact electrical conductivity [90]. The reduction in electrical conductivity is caused by the increasing oxygen content since oxygenated functional groups on the biochar surface are involved in the adsorption process. Contrary, biochar with decreasing particle size is suitable for electrochemical sensing, as electrical percolation thresholds in carbon-filled polymers have been established to decrease with decreasing particle size. Therefore, it is necessary to modify the surface functionality and the porosity according to their intended application.

Moreover, the regeneration of the adsorbent makes the adsorption/detection process economical. This step may involve the use of some reagents, such as NaOH, H₂SO₄, HCl, benzene, acetone, or methanol. However, thermal or microwave regeneration seems to be the more mature regeneration process with low cost and high economic applicability.

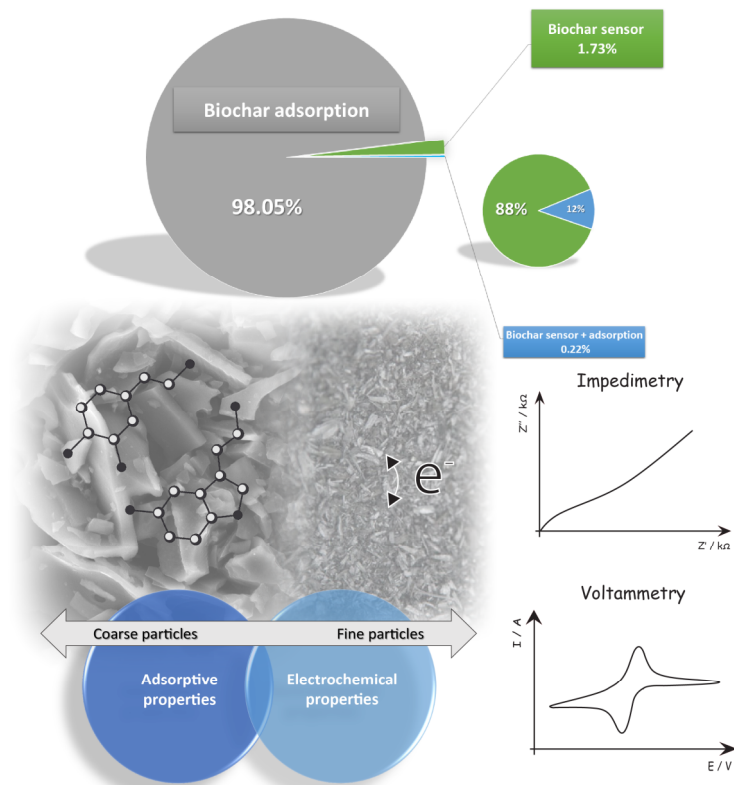


Figure 4. (up) Percentual share of the search on terms “Biochar adsorption”, “Biochar sensor”, and “Biochar sensor adsorption” using Scopus Database; (down) Dependence of biochar particle size on adsorptive and electrochemical properties.

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